LXXIV.—*The Condensation of Anisaldehyde with Resorcinol.*

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SOME short time ago (this vol., p. 78) we described the condensation products obtained from benzaldehyde and resorcinol, and showed that in the presence of alkali hydroxides the course of the reaction followed that shown by Manasse (*Ber.*, 1894, **27**, 2409) to take place with phenols and formaldehyde. In the present communication we have carried out the same series of reactions, using anisaldehyde in place of benzaldehyde. The reaction is rather slower in this case if the reacting substances are kept at the ordinary temperature, the anisaldehyde being perceptible even after several days; but if the aldehyde and resorcinol are heated with the solution of the alkaline hydroxide in a closed vessel at 80—100° for four hours, the reaction is practically complete.

EXPERIMENTAL.

2: 4-Dihydroxy-4'-methoxybenzhydrol,
 $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H_4 \cdot OMe.$

13.6 Grams of anisaldehyde were heated with a solution of 11 grams of resorcinol in 250 c.c. of water containing 25 grams of sodium hydroxide, in a closed vessel in a water-bath for four hours. The blood-red solution so obtained was then diluted with about its own volume of water and acidified with dilute hydrochloric acid, when a very pale yellow precipitate of the hydrol was obtained. The precipitate was collected, washed with water, and dried. For analysis it was dissolved in boiling amyl acetate and the clear solution filtered into light petroleum, the precipitate being collected and dried:

0.1140 gave 0.2842 CO_2 and 0.0588 H_2O . $C=67.99$; $H=5.73$.

$C_{14}H_{14}O_4$ requires $C=68.29$; $H=5.69$ per cent.

2: 4-Dihydroxy-4'-methoxybenzhydrol, when freshly prepared, is a faintly yellow-coloured solid, which darkens rapidly on exposure to air. It does not melt on heating. It is soluble in glacial acetic acid, pyridine, or amyl acetate, but is insoluble in light petroleum. It is readily soluble in aqueous potassium hydroxide, and the solution, on concentration, yields a reddish-brown *dipotassium* salt, which crystallises from dilute alcohol in small needles:

0.4690 gave 0.2548 K_2SO_4 . $K=24.35$.

$C_{14}H_{12}O_4K_2$ requires $K=24.22$ per cent.

The *diacetyl* derivative was prepared by heating 5 grams of the hydrol with 25 grams of acetic anhydride and 1 gram of zinc dust for three hours under reflux. The solution was filtered from excess of zinc dust and poured into dilute alcohol, and the whole then warmed for some time on the water-bath in order to remove excess of acetic anhydride. The solid product was collected, washed, and crystallised from dilute acetic acid, from which it separated in small, almost colourless needles, which begin to decompose when heated to 120° :

0.1104 gave 0.2643 CO_2 and 0.0556 H_2O . $C=65.29$; $H=5.59$.

$C_{18}H_{18}O_6$ requires $C=65.45$; $H=5.45$ per cent.

The *dibenzoyl* derivative was obtained by dissolving 4.92 grams of the hydrol in the calculated amount of sodium hydroxide (2 mols.) dissolved in 40 c.c. of water, and adding 5.62 grams of benzoyl chloride. The mixture was well shaken, the faintly yellow precipitate collected, washed, and crystallised from dilute acetic acid:

0.1170 gave 0.3190 CO_2 and 0.0534 H_2O . $C=74.36$; $H=5.07$.

$C_{28}H_{22}O_6$ requires $C=74.01$; $H=4.84$ per cent.

It begins to decompose at about 90°.

6-Hydroxy-4'-methoxy-9-phenyl-2-methylxanthen,

—2·46 Grams of the hydrol were mixed with 1·08 grams of *p*-cresol and 1 gram of anhydrous zinc chloride, and the mixture was heated at 160° for four hours. The product was extracted several times with water, and then redissolved in aqueous sodium hydroxide in the presence of a small quantity of zinc dust, the solution filtered, and the xanthen, precipitated by acetic acid, was washed and dried. For analysis, it was dissolved in chloroform, and the solution filtered into light petroleum, when a flocculent precipitate separated, which rapidly darkened on exposure, probably owing to slight oxidation and consequent formation of the corresponding fluorone derivative in slight amount. It melts at 112°:

0·1280 gave 0·3716 CO₂ and 0·0668 H₂O. C=79·17; H=5·80.

C₂₁H₁₈O₃ requires C=79·24; H=5·66 per cent.

The *acetyl* derivative was obtained by heating 2 grams of the xanthen with 2 grams of fused sodium acetate, 10 grams of acetic anhydride, and 1 gram of zinc dust for two to three hours under reflux. The product was poured into dilute alcohol, and warmed on the water-bath for some time to remove excess of acetic anhydride. On cooling, the solid mass was collected, washed, and then recrystallised from dilute acetic acid. It melts and decomposes at about 130—135°:

0·1084 gave 0·3042 CO₂ and 0·0550 H₂O. C=76·54; H=5·64.

C₂₃H₂₀O₄ requires C=76·66; H=5·55 per cent.

3: 6-Dihydroxy-4'-methoxy-9-phenylxanthen,

was prepared in a similar manner by heating 2·46 grams of the hydrol with 1·1 grams of resorcinol at 160° for four hours. The product was extracted with hot water, and the residue recrystallised from dilute alcohol, from which it separates in small needles:

0·1080 gave 0·2966 CO₂ and 0·0504 H₂O. C=74·9; H=5·18.

C₂₀H₁₆O₄ requires C=75·00; H=5·00 per cent.

The *diacetyl* derivative was obtained by heating 2 grams of the xanthen with 2 grams of fused sodium acetate, 1 gram of zinc dust, and 10 grams of acetic anhydride for two hours. The product was poured into dilute alcohol, heated on the water-bath to remove excess of the anhydride, the solution cooled, and the precipitate collected and well washed with water. It was then dissolved in hot glacial acetic acid, water added until a faint turbidity was produced, a little zinc dust was also added, and the solution then filtered.

On cooling, the diacetate separated as a colourless, crystalline powder, which melted and decomposed at 140–150°:

0.1100 gave 0.2882 CO₂ and 0.0504 H₂O. C=71.45; H=5.09.

C₂₄H₂₀O₆ requires C=71.29; H=4.95 per cent.

8-Hydroxy-11-p-methoxyphenyl-β-naphthaxanthen,*

—2.46 Grams of the hydrol were mixed with 1.44 grams of β-naphthol and 1 gram of anhydrous zinc chloride, and the mixture heated at 160° for three hours. The product was extracted with water, dissolved in sodium hydroxide in the presence of a small quantity of zinc dust, and filtered. The xanthen was then precipitated from its alkaline solution by means of acetic acid, and the precipitate collected, washed, and dried. For analysis, it was dissolved in chloroform, and the clear solution then filtered into light petroleum, when it separated as a red-coloured, crystalline powder, which melted at 120°:

0.1048 gave 0.3120 CO₂ and 0.0482 H₂O. C=81.11; H=5.11.

C₂₄H₁₈O₃ requires C=81.36; H=5.08 per cent.

The *acetyl* derivative was prepared in a similar manner to that used in the case of the other xanthen, and for analysis was dissolved in chloroform and precipitated by the addition of light petroleum. It was thus obtained as a brown-coloured powder, which melts at 95°:

0.1074 gave 0.3095 CO₂ and 0.0492 H₂O. C=78.59; H=5.01.

C₂₆H₂₀O₄ requires C=78.79; H=5.05 per cent.

8-Hydroxy-5-p-methoxyphenyl-3-methyldihydroacridine,

—This substance was prepared by heating 2.46 grams of the hydrol with 1.07 grams of *p*-toluidine for four hours at 160°. The product was extracted with water, collected and washed, and then dissolved in sodium hydroxide solution in the presence of a small quantity of zinc dust. The solution was filtered, and the dihydroacridine precipitated by the addition of acetic acid, collected, washed, and dried. For analysis, it was dissolved in benzene, and precipitated from the benzene solution by the addition of light petroleum. It separates as an almost colourless, microcrystalline powder, but soon becomes reddish-brown on exposure to air. It melts at 110°:

0.1180 gave 0.3442 CO₂ and 0.0654 H₂O. C=79.55; H=6.16.

0.1920 „ 7.6 c.c. N₂ (dry) at 17° and 750 mm. N=4.60.

C₂₁H₁₉O₂N requires C=79.49; H=5.99; N=4.41 per cent.

* Compare this vol., p. 82.

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The *acetyl* derivative was prepared in the usual way by heating the hydroacridine with acetic anhydride and fused sodium acetate in the presence of zinc dust. The product was poured into dilute alcohol, and warmed to remove the excess of anhydride. It was then dissolved in glacial acetic acid, the solution poured into water, and the resulting precipitate collected, washed, and dried. For analysis it was dissolved in benzene and reprecipitated by the addition of light petroleum, when it separated in minute, almost colourless needles, decomposing at 140° :

0.1086 gave 0.3048 CO_2 and 0.0532 H_2O . $\text{C}=76.55$; $\text{H}=5.44$.

0.1860 „ 6.8 c.c. N_2 (dry) at 17° and 740 mm. $\text{N}=4.19$.

$\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=76.88$; $\text{H}=5.85$; $\text{N}=3.90$ per cent.

10-*Hydroxy-7-p-methoxyphenyldihydro- $\alpha\beta$ -phenonaphthacridine*,

—2.46 Grams of the hydrol were heated with 1.43 grams of β -naphthylamine for four hours at 160° . The product was extracted with water, dissolved in glacial acetic acid in the presence of a small quantity of zinc dust, filtered, and reprecipitated by the addition of water. It was collected, washed and dried, and then dissolved in benzene and reprecipitated by the addition of light petroleum, when it separates as a nearly colourless, crystalline powder, which darkens on exposure:

0.1120 gave 0.3360 CO_2 and 0.0570 H_2O . $\text{C}=81.82$; $\text{H}=5.65$.

0.2502 „ 8.8 c.c. N_2 (dry) at 13° and 743 mm. $\text{N}=4.1$.

$\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=81.87$; $\text{H}=5.38$; $\text{N}=3.97$ per cent.

The *acetyl* derivative was prepared in the usual manner, and crystallises from dilute acetic acid as an almost colourless powder, decomposing at 110° :

0.1038 gave 0.3000 CO_2 and 0.0516 H_2O . $\text{C}=78.82$; $\text{H}=5.52$.

0.2533 „ 8.4 c.c. N_2 (dry) at 20° and 746 mm. $\text{N}=3.79$.

$\text{C}_{26}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=78.99$; $\text{H}=5.31$; $\text{N}=3.54$ per cent.

As we had not prepared the corresponding dihydroacridine from 2:4-dihydroxybenzhydrol at the time of our last communication, we describe it here.

10-*Hydroxy-7-phenyldihydro- $\alpha\beta$ -phenonaphthacridine*,

—Three grams of 2:4-dihydroxybenzhydrol were heated with 2 grams of β -naphthylamine and 2 grams of anhydrous zinc chloride for four hours at 200° . The product was purified as in the case of

the compound just described, and purified for analysis by solution in chloroform and reprecipitation with light petroleum. It is obtained as a red, flocculent precipitate, which is easily soluble in benzene, chloroform, pyridine, or alcohol. It melts at 116° :

0.1200 gave 0.3754 CO_2 and 0.0584 H_2O . $\text{C} = 85.32$; $\text{H} = 5.41$.

0.3840 „, 15.4 c.c. N_2 (dry) at 17° and 750 mm. $\text{N} = 4.66$.

$\text{C}_{23}\text{H}_{17}\text{ON}$ requires $\text{C} = 85.45$; $\text{H} = 5.26$; $\text{N} = 4.33$ per cent.

The *acetyl* derivative was prepared in the usual manner; it crystallises from alcohol as an almost colourless, microcrystalline powder, which decomposes when heated to 100° :

0.1000 gave 0.3010 CO_2 and 0.0472 H_2O . $\text{C} = 82.09$; $\text{H} = 5.24$.

0.2573 „, 8.6 c.c. N_2 (dry) at 12° and 743 mm. $\text{N} = 3.91$.

$\text{C}_{25}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C} = 82.19$; $\text{H} = 5.21$; $\text{N} = 3.84$ per cent.

The fact that the hydroxyxanthen and dihydroacridines mentioned above cannot be obtained colourless is, we think, due to the fact that oxidation of these substances takes place very rapidly, with consequent production of a certain amount of the corresponding fluorone and acridine derivatives, since we find that these fluorones and acridines are highly coloured substances.

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